Indian J. Phys. **68A** (3), 271 – 278 (1994)

I J P A
— an international journal

Theoretical aspects of doping in tin oxide thin films

S R Vishwakarma, Rahmatullah*, A K Yadav, H C Prasad and M Mishra
Department of Physics, University of Gorakhpur, Gorakhpur-273 009, India

Received 11 December 1991, accepted 16 March 1994

Abstract : In present investigation an attempt has been made to calculate crystalline ionicity for tin oxide and doped tin oxide. The value of crystalline ionicity for tin oxide has been found positive and less than unity. Hence undoped tin oxide possesses predominant covalent bond and exhibits semiconducting behaviour. It is found that when fluorine or chlorine substitutes oxygen or arsenic, phosphorus and antimony substitute tin, the value of crystalline ionicity decreases as compared to the undoped tin oxide system This indicates that doping, either due to tin or oxygen substitution, leads to more predominant covalent situation, hence results higher electrical conductivity. This is in agreement with the observed electrical conductivity of undoped and doped tin oxide thin films.

Keywords Transparent semiconducting oxide, tin oxide, effect of doping, electrical conductivity.

PACS Nos. : 61.72.Vv, 72.80.Ey

1. Introduction

Tin oxide (SnO_2) is wide band gap, n-type semiconducting oxide having nearly metallic conductivity, good transparency in the visible region and high reflectance in IR region in the form of thin solid films. Its electrical conductivity increases when tin oxide is doped with antimony [1], phosphorus [2], arsenic [3], fluorine [4] and chlorine [5]. Deviation from stoichiometry is responsible for high electrical conductivity in transparent semiconducting oxides. A completely stoichiometric oxide would be ionic conductor [6]. In tin oxide its high electrical conductivity results due to the creation of oxygen vacancies *i.e.* non-stoichiometry in the crystal [7] during the fabrication of the films. When an oxygen atom removes, two electrons of the oxygen ion are left in the crystal. If these two electrons are localised at the oxygen vacancy, the charge is same as in a perfect crystal and the vacancy has the zero

* Z A Islamic College, Siwan-841 226, India

effective charge. Such vacancies are neutral. If one or both of the localised electrons are excited and transferred away from the vacancy, the vacancy is left with an effective positive charge with respect to the perfect crystal. The charged vacancy becomes an electron trapping site and in this process one or more electrons are available for conduction. If cation is multivalent (*i.e.*Sn) the creation of too many oxygen vacancies results in a structure change from SnO_2 to SnO [8]. The typical free electron concentration is found to be in the range of about 10^{23} to 10^{27} m^{-3} when the number of charged vacancies is small (1%). If instead of creating oxygen vacancies by chemical reduction, cations with a valence higher than that of host, are substituted into the host lattice, then it is electrically same as creating anion vacancies. Since overall the charge neutrality must be preserved, substitution of higher valent cation requires for the addition of an electron. As with oxygen vacancies, not all higher valent dopants incorporated into the lattice produce charge carriers. Some simply remains as neutral point defects. Electrically equivalent effects can occur if anion sites are substituted with atoms whose valence is lower than that of oxygen. The increase in electrical conductivity is observed by doping when the dopant ions replace the appropriate host ion substitutionally in the host lattice. This implies that the ionic radius of the dopant must be of the same size or smaller than the ion it replaces and no compound or solid solution of dopant compound with host oxide is formed. If dopant ion is too large, an interstitial rather than a substitutional site is favoured and dopant will act as a scattering site rather than a source of charge carriers. In doped tin oxide, antimony [9], phosphorus [10] and arsenic [11] are found to substitute tin atom and act as substitutional impurity and donate their extra electrons which give rise *n*-type semiconductivity. The ionic radius of Sn^{4+} is 0.71 Å [12] and that of dopants Sb^{5+}, P^{5+} and As^{5+} are 0.62 Å, 0.34 Å and 0.47 Å [12] respectively. This makes substitution of dopants easier, furthermore arsenic and phosphorus have not found to form any oxide [3], [13] in the host lattice during the fabrication of tin oxide thin films. However, in few rare cases, antimony forms antimony oxide [1] but in general antimony does not form oxide. The doping at anion sites fluorine F^{1-} [14] and chlorine Cl^{1-} [5] are most often used.

2. Theoretical aspects

Theoretical studies (quantitatively or semiquantitatively) regarding the relationship between the type of semiconductivity and the number of free electrons (carriers) in these system (undoped and doped tin oxide) have not been developed so far. Some semiempirical rules in terms of atomic and crystal ionicity of semiconducting compound exists, from which some conclusion regarding the behaviour of dopants in doped system can be drawn. The two conditions under which semiconductivity appears [15] are :

(i) The existence of covalent bonding scheme compatible with crystallographic structure.

(ii) The parameter, crystal ionicity (λ) is positive.

Therefore, an attempt has been made to calculate crystalline ionicity for tin oxide and compared it with the system when it is substituted by Sb, As and P in place of tin or when

oxygen is substituted by F and Cl. The crystalline ionicity is calculated in the following manner :

Let us consider a single M-X bond, in isolation from the other bonds which each of the atoms M and X may form. The extreme electronic distributions are shown schematically in Figure 1(a). Suppose $5\phi_{ms}$ and $2\phi_{xp}$ are the atomic orbital wave functions which represent

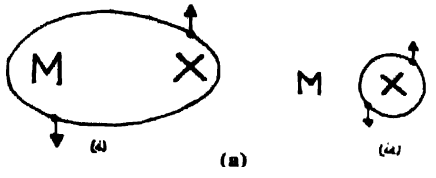

Figure 1. (a) (i) Covalent, (ii) ionic, electron distribution.

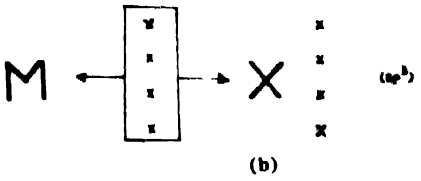

Figure 1. (b) Bonding scheme for hybridized orbitals.

the states of the electrons in these two atoms when separated by infinity. We shall make the following assumptions.

(i) $5\phi_{ms}$ and $2\phi_{xp}$ are the orthogonal wave functions.

(ii) A bonding orbital can be formed by the product of $5\phi_{ms}$ and $2\phi_{xp}$.

(iii) The electrons 1 and 2 of each shared pairs although indistinguishable in a purely covalent distribution, do not play here the same role since M and X are not identical.

(iv) The atom X always plays the role of anion in the ionic distribution. Thus, the wave function for M-X system is given as [16]

$$= a\psi_{cov} + b\psi_{ion}$$

$$= a\left[5\phi_{ms}(1)\ 2\phi_{xp}(2)\right] + b\left[2\phi_{xp}(1)\ 2\phi_{xp}(2)\right]$$

$$= \left[a5\phi_{ms}(1) + b2\phi_{xp}(1)\right] . \left[2\phi_{xp}(2)\right] \qquad (1)$$

The C shared bonding pairs formed by an atom with its near neighbours make up the $2C$ valence electrons participating in the bonds. Let us suppose that the state of half of them is described by the first bracket of E_q (1) (nomadic electrons) and that of the other half by the second bracket (sedentary electrons). Figure 1(b) illustrates that concept for sp^3 hybridisation and bonding scheme for the hybridized orbitals.

The number of bonding electrons whose state is represented by the orbital $5\phi_{ms}$ may be written as $(1 - \lambda)$ per bond, that is $c(1 - \lambda)$ in all (nomadic electrons), whilst the number of those whose state is represented by $2\phi_{xp}$ is then (nomadic electrons +1) per bond (sedentary electrons), that is $c(1 + \lambda)$ in all. More simply we can say that the bonding electrons are distributed as $c(1 - \lambda)$ on the atom M, $c(1 + \lambda)$ on the atom X in an extended crystal MX. We

can also say that $(1 - \lambda)$ and λ are the respective probabilities of the covalent and ionic electron distributions symbolized in Figure 1(a).

In order to evaluate the electron distribution probabilities, we shall proceed in two distinct steps [16]. Let us first suppose that we have constructed an array of neutral atoms having the same co-ordination as in the real crystal. One can imagine this by considering the crystal to be expanded so that interatomic distances are large and each atom may be considered as isolated. The number of bonding electrons that these atoms possess is known. The atom M is completely denuded of these electrons in the ionic scheme; the number of bonding electrons that it possesses is thus equal to the number which are transferred to the atom X in this scheme, *i.e.* n. As there are total $2C$ bonding electrons, $2C - n$ of them remain with atom X. Let us equate this distribution for a certain value of the parameter λ_0 with previous distribution,

$$n = c(1 - \lambda_o) \text{ on the atom M,} \tag{2}$$

$$2C - n = c(1 + \lambda_o) \text{ on the atom X.} \tag{3}$$

These two equations are satisfied for the same value of

$$\lambda_0 = (1 - n/c), \tag{4}$$

where λ_0 is known as atomic ionicity. The values of λ_0 only depend on the position of the atoms M and X in the periodic classification and on the type of bond (trigonal, tetragonal etc).

Now let us consider the real crystal. We obtain it from the dilated crystal above by bringing the atoms closer to one another. Iono-covalent bonds are established between them and these are accompanied by a transfer of electron due to mutual polarisation of the electron clouds. We shall designate by q the number of electrons thus transferred to an atom X by the c, atoms M which surround it, or by q' the number of electrons transferred to an atom M by the C atoms X which surround it (this is a 'chemical' effective charge). It is clear that the fictitous charges m and n give limits for these numbers

$$q \leq n \text{ if } q > 0 \quad \text{[transfer from M to X]}$$

$$q \leq m \text{ if } q < 0 \quad \text{[transfer from X to M].}$$

We shall call q and q' the effective charges carried by the atoms M and X, in contrast to the fictitious charges m and n. The number of bonding electrons associated with atom X in the dilated crystal has been found to be $c(1 + \lambda_0)$. It is now augmented by a quantity q

$$c(1 + \lambda) = c(1 + \lambda_0) + q. \tag{5}$$

This gives a relationship for the calculation of the probability or the crystalline ionicity [17]

$$\lambda = \lambda_0 + q/c. \tag{6}$$

The value of λ is obtained by adding to the atomic ionicity λ_0 a correction for polarity which is nothing more than the displaced charge per bond (q/c).

The empirical formulae for the evaluation of the effective charges [18] are

$$\text{cation} : q = n\left[1 - 0.01185\,(z/r' + z'/r)\right], \tag{7}$$

$$\text{anion} : q' = -n'\left[1 - 0.01185\,(z/r' + z'/r)\right]. \tag{8}$$

Where z and r are the total number of electrons and the ionic radii of atoms present. Primed values refer to the atoms occupying the anion sites. The value of λ lies between zero to one and negative. The value $\lambda = 1$ represents purely ionic crystal and positive value λ between zero and one indicates prominance of covalent character of bond linking in the system. A negative value of λ would correspond to the transfer of sedentary electrons from X towards M which is incompatible with original hypothesis. It is particularly noteworthy the negative values of λ correspond, without any exceptions, to metallic properties of the crystal. In present investigation, using the formulae (4) and (6) λ_0 and λ have been calculated for tin oxide and doped tin oxide with arsenic, antimony, phosphorus, fluorine and chlorine. The values of λ_0 and λ for undoped and doped tin oxide are given in Table 1. The calculated effective charges of anion and cation are also given in Table 1.

Table 1. Variation of crystalline ionicity λ with anionic and cationic doping element in tin oxide.

Ser. no.	Bond system	Atomic ionicity λ_0	Cationic effective charge q	Anionic effective charge q'	Crystalline ionicity λ
1	Sn–O	0.50	1 28	- 0.64	0 82
2	Sn–Cl	0.50	0 80	- 0 80	0 70
3	Sn–F	0.50	0.88	- 0.88	0.72
4	As–O	0.50	1.02	- 1.02	0.75
5	Sb–O	0 50	0.84	- 0.84	0 71
6	P–O	0.50	1.14	- 1.14	0.78
7	As–Cl	0.50	0.70	- 0.70	0.67
8	As–F	0.50	1.02	- 1 02	0.75
9	Sb–Cl	0.50	0.72	- 0.72	0.68
10	Sb–F	0.50	0.82	- 0.82	0 70
11	P–Cl	0.50	0.64	- 0.64	0.66
12	P–F	0.50	1.14	- 1.14	0.78

3. Conclusion

The values calculated for different systems (Sn–O, P–O, As–O, Sb–O, Sn–Cl, Sn–F, Sb–Cl, Sb–F, As–F, P–Cl and P–F) are found to be positive and less than unity (Table 1). Hence, undoped and doped tin oxide possess predominant covalent bond and exhibit semiconducting

behaviour. It is further observed that when F and Cl substitute oxygen or As, Sb and P substitute tin, the value decreases as compared to undoped tin oxide system. This also indicates that the doping either due to tin or oxygen substitution, leads to more predominated covalent situation and shows better semiconductivity or higher electrical conductivity. This is in agreement with observed electrical conductivity data for undoped tin oxide [4], arsenic [3], antimony [1] phosphorus [13], fluorine [4] and chlorine [5] doped tin oxides. As matter of fact the substitution of impurity in place of tin or in place of oxygen changes the matrix of tin oxide as shown in Figure 2.

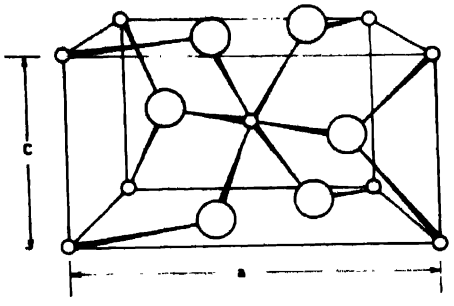

Figure 2. Unit cell of crystal structure of SnO_2. Large circles indicate oxygen and small circles indicate tin atoms. Sn is replaced by As or Sb or P and O atom is replaced by F or Cl.

Basically, there are two processes which control the nature of bonds and charge distribution between the two atoms. The first one due to sharing of charges between the two dissimilar atoms leading covalent bonds. Secondly, electrons donated by substitutional impurity or electron freed due to non-stoichiometry of tin oxide arising from the creation of vacancies at oxygen site. The concept of the covalent bond is defined for identical atoms of the elements but due to the non-stoichiometry of tin oxide, the pure ionic bond does not exist in tin oxide, the ionic bond deviates towards covalent bond. The doping in tin oxide is also responsible for deviation from ionic character to covalent character. The wave function of valence electron may be put into the form [19]

$$: C_1 \psi_{cov} + C_2 \psi_{ion}. \tag{9}$$

This shows that in considering each compound, we could identify the extreme covalent and ionic configurations and the distribution of the electrons in such formulae. The purely ionic bond presents no difficulty since the distribution is fixed by the octet rule. However the case of the covalent bond is more complicated. In the case of doped tin oxide system, the covalent bonds of an impurity atom of arsenic (As^{5+}), antimony (Sb^{5+}) and phosphorus (P^{5+}) are also taking part in the sp^3 orbital hybridization with tin atoms. In general such a notation for the extreme covalent configuration presupposes the excitation of certain electrons of M or X atoms to higher energy levels as well as the transfer of electronic formulae of the isolated atoms, such as transfer taken place in the opposite direction to that required for the ionic bond. The energy required for this process as for the excitation of the electrons, must be balanced by the high bond energies of the orbital hybrid covalent bonds, and more specially

in this case, by the high energies of the intermediate ionocovalent bonds. This notation for the pure covalent bond is predicting semiconductivity in crystal lattice. It is essential to note that the charges introduced for the ionic configurations and for the covalent configurations are quite fictitious *i.e.* they do not allow prediction of the actual sign of the dipole of a bond. The idea about the ionic character can be understood by considering [16], the some fraction of valence electrons are susceptible to be bound to either atom M or to atom X, according to the covalent configuration $M^{m-}X^{m+}$ or ionic configuration $M^{n+}X^{n-}$. This nomadic electrons population $c = m + n$ is also equal to the covalent co-ordination. If we consider for tin oxide or doped tin oxide the nomadic population c will be four due to sp^3 hybridization for tetragonal bonds ($1s + 3p$). The parameter λ crystalline ionicity is also known as the function of nomadic electron bound to X atom, X-ray diffraction and scanning studies [13], [3] reveal information about charge distribution near the atomic site. Hence it also gives information regarding bond formation in transparent conducting oxide system. The different preferred orientation obtained for undoped and doped tin oxide thin films are given in Table 2. It also indicates that the change in the electronic charge distribution is due to different substitutional doping.

Table 2. Preferred orientation of undoped and doped tin oxide films.

Ser. nos.	Doping elements	Preferred orientation	References
1	Nil	< 211 >	20
2	F	< 200 >	21
3	Sb	< 110 >	22
4	P	< 110 >	13
5	As	< 200 >	3

The above semiempirical formula based on calculation of crystalline ionicity λ and its correlation with covalency and electrical conductivity explain the observed results satisfactorily. However, a more exact theory and a closed form of relationship between electrical conductivity, crystal ionicity and electron charge density have yet to be worked out and then the observed results can be explained qualitatively in a more exact manner. We may then get the exact explanation about preferred orientation under different doping condition, the number of charge carriers, varying electrical conductivity with same condition.

Acknowledgments

The author S R Vishwakarma (RA) is thankful to Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial assistance.

References

[1] J Kane, H P Schweizer and W Kern *J. Electrochem. Soc.* **123** 270 (1976)

[2] S Tatsuyama and Ichimura *I L Nuovo Cim.* **38B** 352 (1977)

[3] S R Vishwakarma, J P Upadhyay and H C Prasad *Thin Solid Films* **176** 99 (1989)

[4] J C Manifacier, L Szepessy, J F Bresse and R Stuck *Mater. Res. Bull.* **14** 163 (1979)

[5] A K Abbas *Solid State Commun.* **61** 507 (1987)

[6] N F Mott and R W Gerney *Electronic Process in Ionic Crystal* (London and New York : Oxford Univ Press) (1948)

[7] P Kotstad *Non-stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxide* (New York Wiely) (1972)

[8] C Wagner *J. Phys. Chem. Solids* **33** 1051 (1972)

[9] T Feng, A K Ghosh and G Fishman *J. Appl. Phys.* **50** 8070 (1979)

[10] T Arai *J. Phys. Soc. Jpn.* **38** 916 (1960)

[11] Y S Hsu and S K Gandhi *J. Electrochem. Soc.* **126** 1434 (1979)

[12] J A Dean *Lanje's Hand Book of Chemistry* (New York : Mc Graw-Hill) **3** p 118 (1973)

[13] J P Upadhyay, S R Vishwakarma and H C Prasad *Thin Solid Films* **169** 195 (1989)

[14] G Mavrodiev, M Gajdardziska and N Novkovsi *Thin Solid Films* **113** 93 (1948)

[15] E Mooser, W B Pearson and Rugby *Rep Meeting Semiconductors Phys. Soc* (1956)

[16] J P Suchet *These d' Etat. (Paris)* (1961)

[17] J P Suchet *Proc. Int. Conf. Semiconductor Physics (Prague 1960) Zech J. Physics* 904 (1961)

[18] J P Suchet *J. Phys. Chem. Solids* **21** 156 (1961)

[19] Y K Surkin and M E Dyatkina *Structure of Molecules and the Chemical Bond* (London · Inter Science) (1950)

[20] K B Sundaram and G K Bhagawat *Thin Solid Films* **78** 35 (1981)

[21] M Fantini and I Tornani *Thin Solid Films* **138** 255 (1986)

[22] Titilayo A Kuku *Thin Solid Films* **142** 241 (1986)